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## GEOCHEMISTRY OF THE CLEVELAND MEMBER OF THE OHIO SHALE, APPALACHIAN BASIN: INDICATORS OF DEPOSITIONAL ENVIRONMENT DURING SEDIMENT ACCUMULATION

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### ABSTRACT

Conditions that existed during accumulation of the Devonian Ohio Shale of the Appalachian Basin, and in particular the degree of anoxia, have been debated widely. In this study, two spatial transects that include the Cleveland Member of the Ohio Shale (Famennian, Upper Devonian) are investigated using geochemical proxies (C, S, and trace-elements) to elucidate paleo-depositional environments. One transect extends from the south-central section to the northeastern section of the Kentucky Devonian outcrop belt, and the other extends from central Kentucky northwards into central and northern Ohio. The transect approach defines spatial variability in the redox characteristics that existed across the Appalachian Basin during a unique episode in Earth history.

Results indicate that for these very organic-carbon rich shales (which contain up to 15% organic carbon), redox conditions likely varied both spatially and temporally. The upper Cleveland contains more organic carbon than does the lower Cleveland, and the overall carbon content decreases toward the northernmost part of our study area (northern Ohio). Associated with these variations in organic carbon are redox differences, in that conditions during accumulation of the lower part of the Cleveland Shale Member may have been slightly better oxygenated (dysoxic) compared with those that existed during accumulation of the upper parts of the unit (anoxic). This is demonstrated by vertical variations in  $DOP_T$ , V/Cr, and Ni/Co. Redox conditions also vary from core to core, suggesting local fluctuations may have been important; data for the northernmost (or most proximal) core suggest the least reducing conditions.

Mo contents are generally high in these cores (averaging between 80 and 125 ppm for various cores). Some cores demonstrate a decrease in Mo content in the upper part of the Cleveland Shale Member whereas others do not, suggesting local control on Mo content rather than a global or basin-wide drawdown of seawater Mo levels during accumulation of the upper Cleveland.

### Introduction

Devonian organic-rich black shales of the Appalachian Basin have been studied extensively in terms of depositional environments, stratigraphy, and tectonics (for example, Ettensohn et al., 1979; Ettensohn and Barron, 1981; Ettensohn, 1985 a,b; Schieber, 1998; Murphy, Sageman, and Hollander, 2000; Murphy, Sage-

man, Hollander, Lyons, and Brett, 2000; Murphy, Sageman, Hollander, and Ver Straeten, 2000; Werne et al., 2002; Sageman et al., 2003; Rimmer, 2004; Rimmer et al., 2004). However, the reasons for extensive OM (organic material) accumulation and preservation in these sediments have been debated; in particular there have been different interpretations regarding bottom-water

conditions during sediment accumulation. Ettensohn (1998) proposed accumulation under conditions of sediment starvation and widespread water-column anoxia beneath a permanent pycnocline for high organic-carbon (> 10%) black shales which he considered to be transgressive shales, and which include the Late Devonian lower and upper Huron Member and the Cleveland Member of the Ohio Shale, along with the Early Mississippian Sunbury Shale. For lower organic-carbon (< 10%) shales, which he considered regressive black shales and which include the middle Huron Member of the Ohio Shale, the Three Lick Bed, and the Bedford Shale, Ettensohn (1998) suggested that organic matter accumulation was driven by productivity, possibly enhanced by the influx of terrestrially derived nutrients, but in the absence of widespread water-column anoxic conditions.

A detailed analysis of paleo-redox trace metal indicators by Rimmer (2004) suggested that, at least for Devonian shales in the outcrop belt of Kentucky, bottom-water conditions may have been quite variable. Whereas anoxic conditions may have prevailed during accumulation of some intervals in the upper part of the Cleveland Member, bottom-water conditions may have been intermittently anoxic and dysoxic during deposition of the lower Cleveland. During accumulation of the underlying Huron Member, it is likely that conditions ranged from anoxic to dysoxic to marginally oxic, possibly being close to normal marine conditions at times during accumulation of the lowermost Huron sediments.

Further north in the Appalachian Basin in New York, models have been proposed that invoke only seasonal water-column stratification during deposition of Middle Devonian black shales, such as the Oatka Creek Formation and the Genesee Shale, and that emphasize the importance of nutrient cycling under variable bottom-water conditions that in turn enhances productivity in surface waters following periodic deep-water overturn (Murphy, Sageman, and Hollander, 2000; Murphy, Sageman, Hollander, Lyons, and Brett, 2000; Murphy, Sageman, Hollander, and Ver Straeten, 2000; Werne et al., 2002; Sageman et al., 2003). An analysis of several black shale units from the same core in New York demonstrated that very few of the black shale units were deposited under persistently anoxic or euxinic conditions, and that most accumulated under seasonally stratified water columns (Sageman et al., 2003).

As a major area of debate has been the extent to which these black-shale basins were anoxic or euxinic, and that their redox characteristics potentially varied depending on location within the basin, the purpose of this study is to evaluate redox indicators in the Cleveland Member of the Ohio Shale (Famennian, Upper Devonian) across two transects. One of these transects the outcrop belt of east-central Kentucky, the other passes from central Kentucky into central and northern Ohio. The transect approach allows comparison of redox conditions in the distal areas of the basin (central Kentucky) with those in closer proximity to the Catskill Delta sediment source to the north (i.e., the central and northern Ohio cores).

### Sampling and Methods

#### Stratigraphy

Within the Devonian outcrop belt of east-central Kentucky, the New Albany/Ohio Shale thins onto the Cincinnati Arch to around 40–45 m (130–150 ft) thick. In this area, U.S. Geological Survey 7.5-minute geologic quadrangle maps use both New Albany Shale

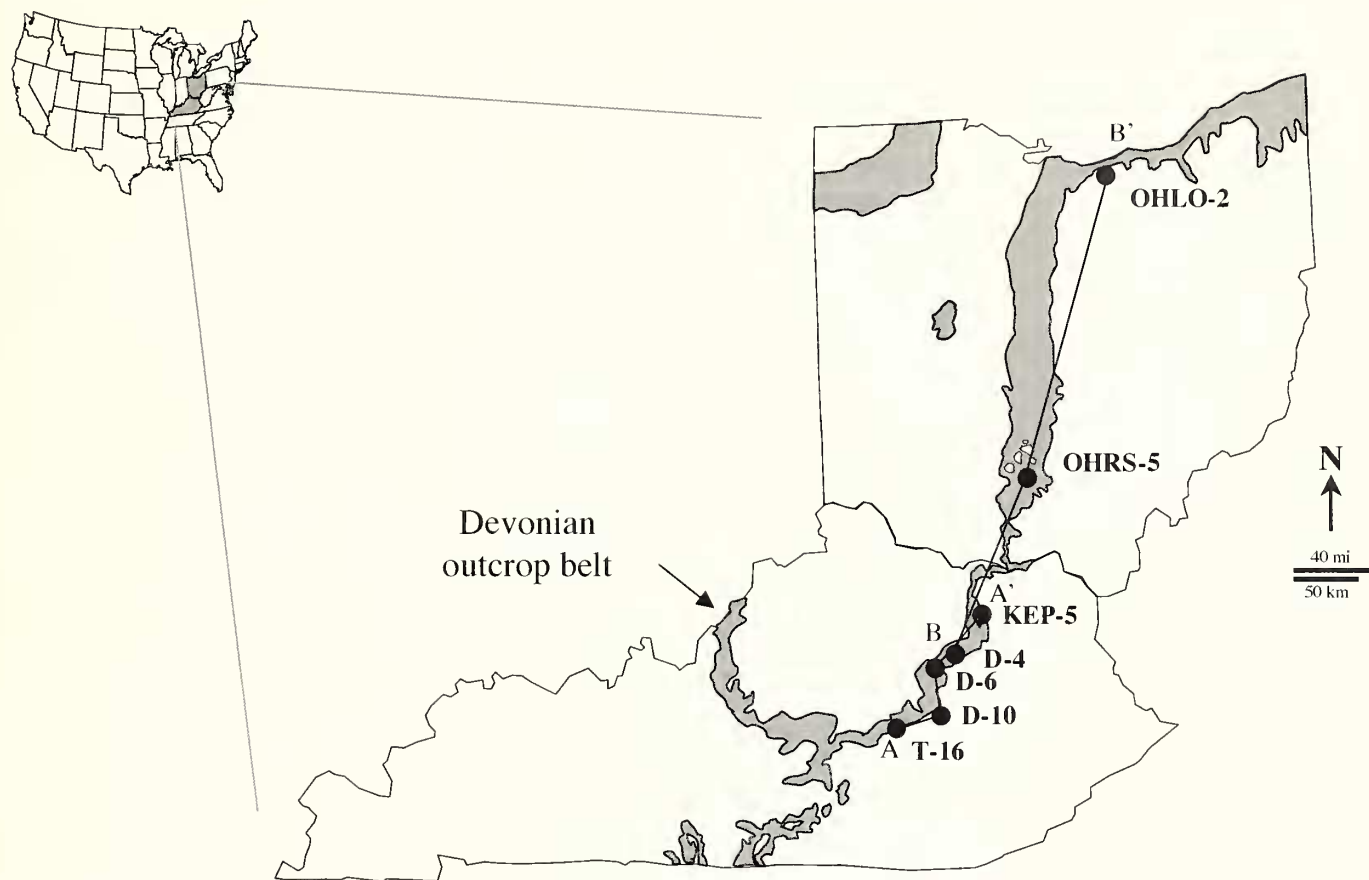
(cores D-6, D-10, and T-16) and Ohio Shale (core KEP-5) terminology. From the outcrop belt, the Devonian shales increase in thickness toward southeastern Kentucky (up to ~ 455m, 1500 ft thick) as they dip down into the subsurface in the Appalachian Basin. Present-day burial depths for the shale increase toward the southeast, reaching ~ 730m (2400 ft) in southeastern Kentucky. Even greater thicknesses and burial depths are seen in West Virginia (Provo, 1977). From Kentucky, the outcrop belt continues northwards into Ohio where in central Ohio, the Ohio Shale averages 140 m (460 ft) thick and increases to over 400 m (1312 ft) thick in the northeastern part of the state (Hellstrom and Babcock, 2000).

In central Kentucky, the Ohio Shale/New Albany Shale consists of the Cleveland and the Huron members, separated by the Three Lick Bed (a number of interbedded siltstones and shales). In this area, the upper part of the Cleveland Member is typically a black (N1) or grayish-black (N2) laminated shale, with occasional olive black laminae (5Y 2/1), whereas the lower part of the Cleveland is typically olive black (5Y 2/1) to brownish gray (5YR 2/1) (Pollock et al., 1982). Within the unit, pyrite nodules occur as do phosphate nodules and cone-in-cone limestone. The unit, bounded by the Bedford Shale and the Three Lick Bed, increases in thickness across transect A–A' (Figure 1), from approximately 7.6 m (25 ft) in the south (core T-16) to over 15 m (50 ft) in the north (KEP-5) (Figure 2). The Three Lick Bed is identifiable into central Ohio, but toward northern Ohio, the Cleveland Member is separated from the Huron Member by the Chagrin Shale Member, thought to be, in part, correlative with the Three Lick Bed observed to the south (Hellstrom and Babcock, 2000). In the northern part of Ohio, the Cleveland Member is a dark grey (N3 to N5) shale, typically microlaminated, and with occasional cone-in-cone limestone. In the area studied, the Cleveland is approximately 23 m (75 ft) thick. Stratigraphic correlation was based on driller's logs, input from state survey personnel, and comparison of gamma logs to those in the literature (for example, Hellstrom and Babcock, 2000).

#### Sampling

For the central Kentucky transect (A–A'), four cores were selected to represent a SW–NE transect along the eastern Devonian shale outcrop belt (Figure 1). These included the T-16 (Madison Co., KY), D-10 (Estill Co., KY), D-6 (Montgomery Co., KY), and KEP-5 (Fleming Co., KY) cores. For these and other cores in the outcrop belt, we have an extensive data base (UK Devonian Shale Database) that includes carbon, sulfur, major and minor elements, and trace-element data for Ohio Shale cores which were generated as part of an evaluation of oil-shale resources in Kentucky in the 1980s at the University of Kentucky's Center for Applied Energy Research (CAER), formerly the Kentucky Center for Energy Research Laboratory (KCERL). These data are being used to evaluate depositional conditions for the black shales in central Kentucky (Rimmer, 2004; Rimmer et al., 2004; Rimmer and Rowe, in preparation). For the four A–A' transect cores, the data were collected on composite samples of the Cleveland Member representing ~ 0.6 m (2 ft) intervals for organic-carbon-rich intervals, or 1.5 m (5 ft) intervals for lean zones.

The second transect (B–B') is defined by one core from central Kentucky (D-4, Bath Co.), one from central Ohio (OHRS-5, Ross Co.), and one from northern Ohio (OHLO-2, Lorain Co.) (Figure 1). For these cores, a different sampling approach was taken, whereby 10 cm (3–4 in) intervals were selected. For each



**Figure 1.** Map showing location of cores used in this study. Transect A–A' is based on data for four cores (T-16, D-10, D-6, and KEP-5) from the UK Devonian Shale Database; transect B–B' includes three cores (D-4, OHRS-5, and OHLO-2) sampled for the purpose of this investigation.

interval, an attempt was made to sample only homogeneous intervals, thus encapsulating more of the small-scale geochemical variability than could be assessed using the larger intervals for data used for transect A–A'.

#### Analytical methods

Results for cores from transect A–A' were obtained from the UK Devonian Shale Database. Carbon and sulfur analyses were performed previously based on standard methods (Robl et al., 1983), using a Carlo-Erba Model 1106 elemental analyzer (for carbon) and a Fisher Model 470 sulfur analyzer. Coefficient of variation ( $100 \times$  standard deviation/mean) for replicate analyses was 0.5% for carbon and 2% for sulfur (Robl et al., 1983). Trace elements were determined by x-ray fluorescence, using a Philips AXS automated spectrometer. For samples from transect B–B', organic carbon was determined using a Costech 5010 elemental analyzer following multiple treatments with 50  $\mu\text{L}$   $\text{H}_2\text{SO}_3$  to remove carbonate. Sulfur was determined using a Leco sulfur analyzer. Standard deviations for analyses were 0.05% and 0.01% for carbon and sulfur, respectively. Trace elements were determined by x-ray fluorescence using a Bruker S4 Pioneer, housed at the Kentucky Geological Survey.

For the purposes of calculating the degree of pyritization (DOP),  $S_T$  was assumed to approximate pyritic sulfur ( $S_{\text{pyr}}$ ) as

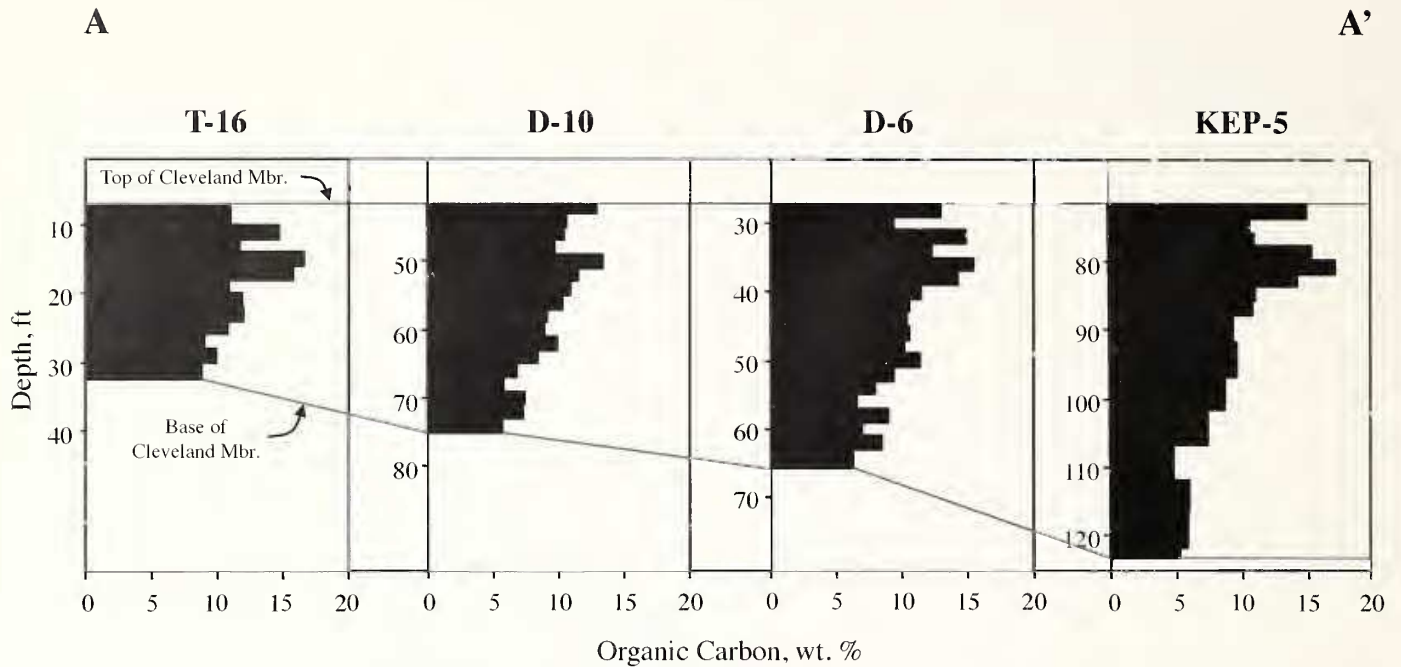
little organic sulfur is thought to be present. Analysis of kerogen concentrates has shown that  $S_{\text{org}}$  constitutes less than 2% of the organic matter (Taulbee et al., 1990). DOP is defined as pyritic iron/(pyritic iron plus HCl-soluble iron) (Berner, 1970). In this study,  $\text{DOP}_T$  was determined from pyritic iron/total iron (Raiswell and Berner, 1986), and pyritic iron was calculated from total sulfur, assuming all of the sulfur was in the form of pyrite.

Redox terms used here—oxic, dysoxic, and anoxic—refer to bottom-water oxygen levels (8.0 to 2.0, 2.0 to 0.2, and 0.0 ml  $\text{O}_2/\text{l}$ , respectively) (Tyson and Pearson, 1991). Euxinic environments are those in which free  $\text{H}_2\text{S}$  is present in the water column (Raiswell and Berner, 1985).

## Results and Discussion

### Carbon-sulfur-iron relationships

Along the Kentucky transect (A–A'), organic carbon contents of the Cleveland Member range from approximately 5% in the lower part of the unit to 12–15% in the upper Cleveland with very similar patterns exhibited in all four cores (Figure 2). These unusually high organic carbon contents suggest that conditions during sediment accumulation were not those encountered under normal marine conditions. The relationship between carbon and sulfur may provide clues as to whether conditions at the time of sediment accumulation were normal marine or euxinic. For



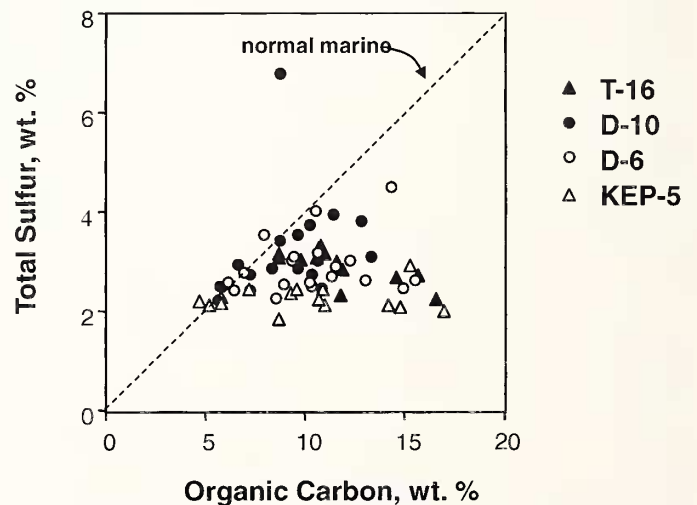
**Figure 2.** Variation in thickness and organic carbon content (wt. %) of the Cleveland Member of the Ohio Shale across transect A–A' in central Kentucky.

sediments that accumulated under oxygenated conditions (normal marine), a crossplot for organic carbon and pyritic sulfur should show a strong positive correlation with the trend line through the data having a zero intercept (Bernier and Raiswell, 1983). This is because pyrite formation in normal marine sediments is controlled by OM availability. In contrast, in euxinic environments, pyrite formation is primarily controlled by iron availability and a plot of  $C_{org}$  versus  $S_{pyr}$  shows a non-zero sulfur intercept (thus higher  $S_{pyr}$  contents are associated with low  $C_{org}$  contents) and may or may not show any correlation between the two variables (Bernier and Raiswell, 1983). Interpretations based on C-S plots could be compromised if there has been a significant loss of carbon accompanying thermal maturity (as discussed by Raiswell and Bernier, 1987). However, the black shales in this part of the Appalachian Basin are relatively immature ( $R_o \sim 0.5\%$ ) (Rimmer et al., 1993; Curtis and Faure, 1997), and therefore C-S plots may be used to evaluate original depositional environment.

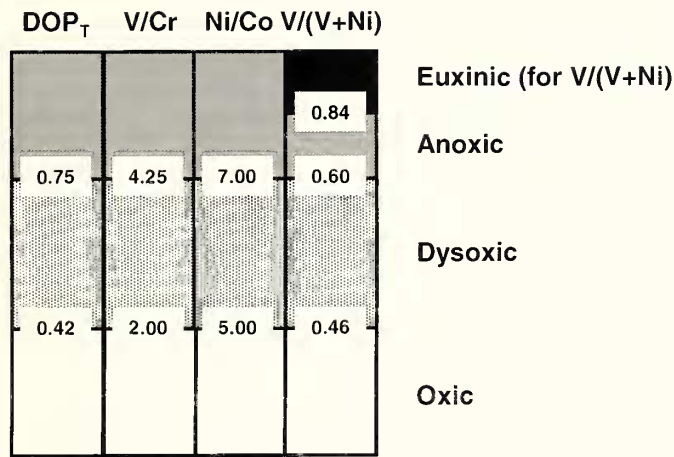
For the four cores along transect A–A', a C-S crossplot shows no correlation between the two variables (Figure 3), suggesting that conditions during sediment accumulation were not normal marine, and possibly anoxic. Further evidence for non-normal marine conditions is provided by the  $DOP_T$  values determined for these samples. Degree of pyritization ( $DOP_T$ ) reflects redox conditions during sediment accumulation:  $DOP$  values less than 0.42 indicate oxic (normal marine) conditions, and values in excess of 0.75 indicate conditions with no oxygen present (anoxic) and possibly  $H_2S$  present (euxinic) (Raiswell et al., 1988) (Figure 4). Values between 0.42 and 0.75 indicate dysoxic conditions although there may be some overlap for values associated with dysoxic and anoxic environments. Raiswell et al. (1988) originally referred to conditions associated with  $DOP$  values  $> 0.75$  as inhospitable, and those associated with values between 0.42 and 0.75 as restricted. Hatch and Leventhal (1992)

suggested that values between 0.67 and 0.75 represent a less strongly stratified water column, whereas values greater than 0.75 represent a strongly stratified, anoxic water column.

$DOP_T$  values for the four cores along transect A–A' suggest a fairly wide range of conditions, from dysoxic to anoxic, but with the majority of the values falling into the dysoxic range (Figure 5). Very few values are consistent with anoxic conditions using the Raiswell et al. (1988) threshold of 0.75; however, if the Hatch and Leventhal's (1992) threshold of 0.67 is used, several



**Figure 3.** Carbon-sulfur relationships for the Cleveland Member in transect A–A'. The dashed line shows the typical S-C relationship for normal marine sediments (based on Bernier and Raiswell, 1983).

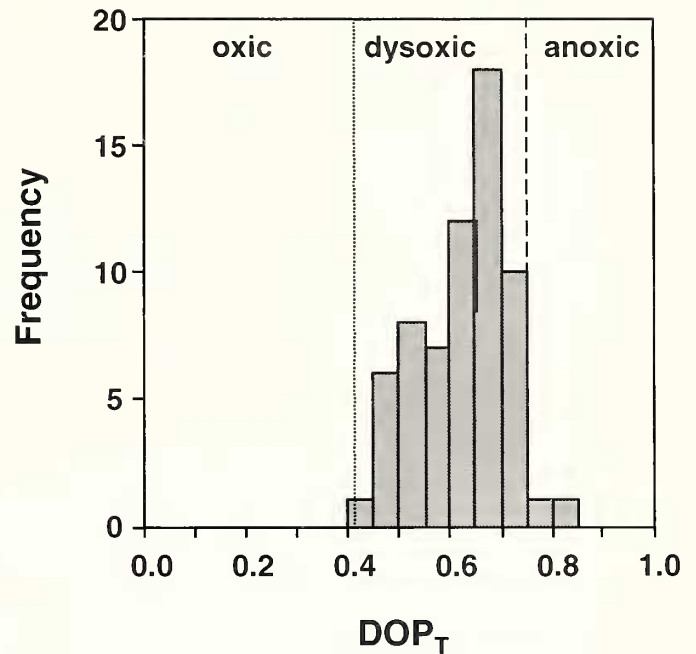


**Figure 4.** Correlation of redox proxies used in this study (modified from Jones and Manning (1994); based on thresholds reported in Raiswell et al. (1988), Hatch and Leventhal (1992), and Jones and Manning (1994).

intervals have values that are high enough to indicate anoxic conditions. Analysis of results for individual cores suggests that evidence exists for lateral variability in DOP<sub>T</sub>: for example, DOP<sub>T</sub> values determined for core T-16 are higher than those observed in core KEP-5 (Figure 6). In both cores, somewhat lower values are observed in the bottom part of the Cleveland Member.

Thus, it appears that C-S-Fe relationships for cores along transect A-A' indicate somewhat variable conditions during deposition of the Cleveland Member. C-S plots suggest that conditions were not normal marine, and may even have been anoxic to euxinic. However, the degree of pyritization suggests dysoxic conditions may have been prevalent, with possibly more anoxic conditions emerging during deposition of some intervals in the upper part of the Cleveland. This is consistent with observations made by Rimmer (2004) and Rimmer et al. (2004) who analyzed results for several cores from the outcrop belt, and those of Robl and Barron (1987) who evaluated C-S relationships for the Cleveland.

Moving north from central Kentucky into central Ohio along transect B-B', organic carbon contents appear to be relatively consistent, ranging from approximately 5% to over 15% in cores D-4 and OHRS-5, and also showing higher organic carbon levels in the upper part of the unit (Figure 7). However, in core OHLO-2 at the northernmost part of our transect, carbon contents throughout the unit are generally lower, ranging from less than 5% up to 10% (Figure 7). The C-S crossplot for transect B-B' shows no relationship between the variables, again suggesting that conditions were not normal marine. DOP<sub>T</sub> values for the D4 core are similar to those determined for the other cores from Kentucky, with most of the values plotting in the dysoxic field and a few in the anoxic field (Figure 7). DOP<sub>T</sub> values for OHRS-5 and OHLO-2 are also mostly dysoxic, but generally lower than those for D-4; several values for these two cores plot in the oxic field. Thus, it appears that based on C-S-Fe relationships, there are differences in redox conditions moving along transect B-B' towards the north: conditions appear to become slightly more oxygenated in northern Ohio than they are in central Kentucky.

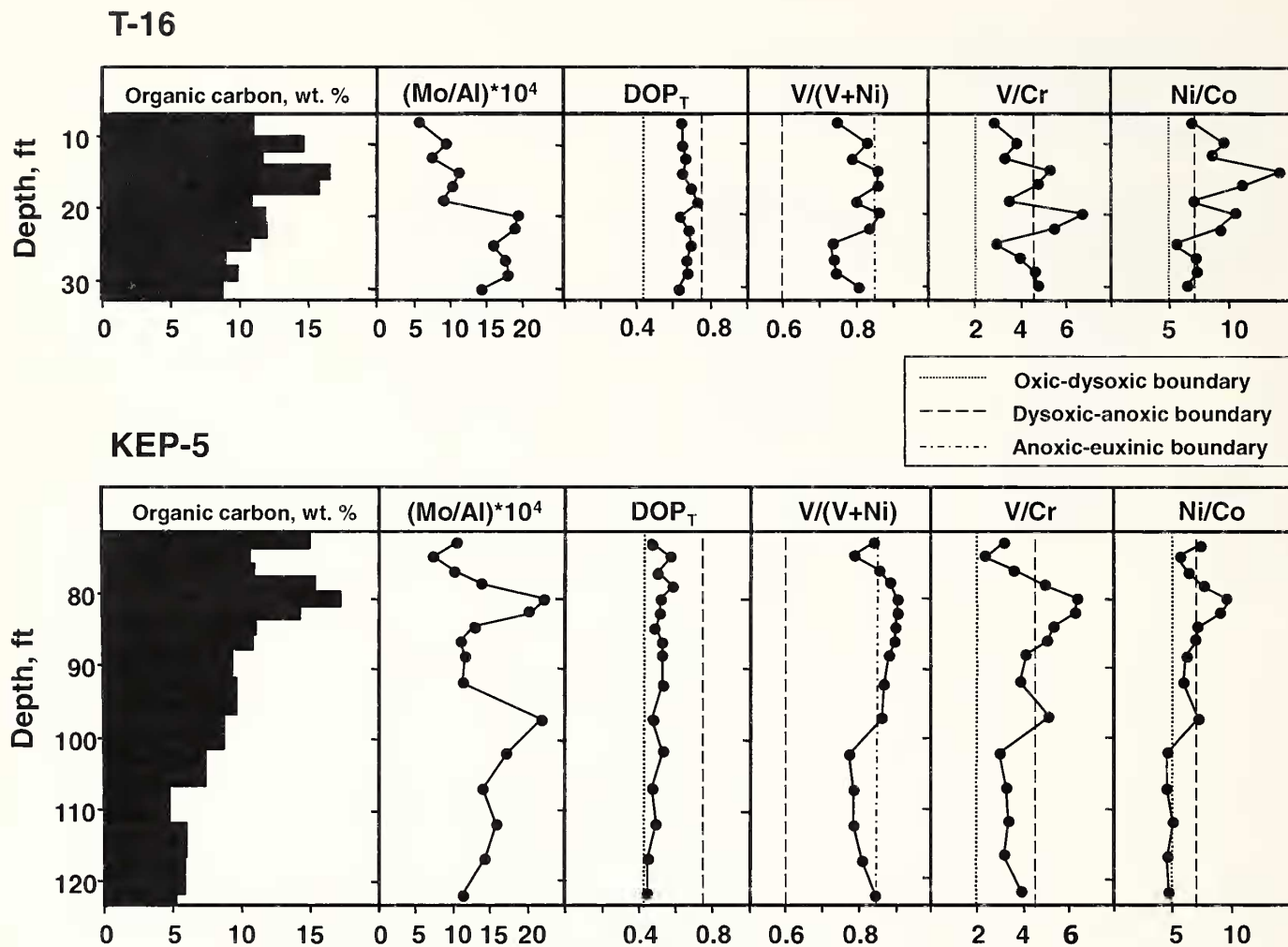


**Figure 5.** Histogram showing the distribution of DOP<sub>T</sub> values determined for cores in transect A-A'.

#### Trace-metal enrichment factors and ratios

Trace-metal concentrations and ratios can also be used to evaluate depositional environments (for example, Breit and Wanty, 1991; Hatch and Leventhal, 1992; Jones and Manning, 1994; Tribouillard et al., 1994). In this study, we focus on a few indices that have been used previously to elucidate depositional environment of organic-rich shales, specifically Mo, V/(V+Ni), V/Cr, and Ni/Co. Thresholds for several of these have been suggested as a means of differentiating between oxic, dysoxic, and anoxic conditions (Hatch and Leventhal, 1992; Jones and Manning, 1994) (Figure 4) and have been applied previously to the Devonian shales of Kentucky (Rimmer, 2004; Rimmer et al., 2004).

Trace metals in general are enriched in these shales. The enrichment factor (EF) for an element is equal to (Element/Al)/(Element/Al)<sub>shale</sub>, where the ratio in the numerator is that for the shale in question, and the ratio in the denominator is that for a "typical" shale (based on averages reported by Wedepohl, 1971). In these shales we see a significant level of enrichment in some trace metals (Table 1), in particular Mo. Overall, enrichment levels relative to an average shale are similar in the two transects: Mo > V > Zn > Cu > Ni > Cr > Co, although in transect B-B', Cu and Ni are in reversed order in terms of enrichment. Some of the differences observed in the enrichment factors for transects A-A' and B-B' may be due to the different sampling approach used for these two transects, thus we limit our comparisons to within each transect. High Mo contents are associated typically with anoxic and euxinic conditions (Dean et al., 1977; Crusius et al., 1996), although some workers have suggested Mo contents as high as 150 ppm may be associated with dysoxic environments (Schultz and Coveny, 1992). Mo data indicate a decrease along transect B-B' suggesting changing conditions toward the north: conditions were at least dysoxic and possibly anoxic (based on Mo levels that average 80 to 100 ppm), but a slight decrease in OHLO-2 suggests less reducing conditions for this most northerly core. At individual



**Figure 6.** Stratigraphic variations in organic carbon (wt. %) and redox proxies for two cores (T-16 and KEP-5) in transect A–A'. Redox thresholds based on values in Figure 4.

locations, there are some apparent vertical changes in Mo content: results for cores D-4 and T-16 show a decrease in Mo in the upper Cleveland. However, this does not appear to be a trend seen throughout the basin: no decrease is observed in KEP-5, OHRS-5, or OHLO-2 and in fact some of the highest Mo levels are observed in the upper part of both KEP-5 and OHRS-5.

Based on thresholds shown in Figure 4, V/Cr and Ni/Co ratios suggest oxidic to dysoxic conditions for the lower part of the Cleveland Member for cores T-16 and KEP-5 (transect A–A'), with dysoxic to anoxic conditions for the upper Cleveland. V/(V+Ni) ratios suggest anoxic conditions for the base and euxinic conditions for the upper part of the section. The discrepancy in redox conditions indicated by these trace-element proxies is consistent with observations by Rimmer (2004) who cautioned against strict use of redox thresholds developed in previous studies and suggested that these ratios should be used in a relative sense. At the very least, using a cautious approach, it is reasonable to suggest that there were differences in redox conditions at the time of sediment accumulation between the lower and upper parts of the Cleveland Member.

For transect B–B', similar values are seen for D-4 and OHRS-5, with differences apparent between the upper and lower parts of the

unit: V/Cr and Ni/Co indicate primarily dysoxic conditions in the lower Cleveland Member, but anoxic conditions in the top of the unit, although the results for OHRS-5 indicate only a slight increase in Ni/Co values in the top of the section. As in the case of the A–A' transect, V/(V+Ni) values indicate more reducing conditions than do V/Cr and Ni/Co. In this transect, trace elements ratios for core OHLO-2 suggest less reducing conditions overall, although they follow similar trends to the two more southerly cores: V/Cr suggests dysoxic (bottom) to anoxic (top) conditions, but most Ni/Co values straddle the range for dysoxic conditions with even a few intervals that fall in the oxidic range. V/(V+Ni) are in the anoxic range, but rarely are high enough to be indicative of euxinic conditions.

#### Redox conditions during accumulation of the Cleveland Member

A much-debated issue surrounding Devonian black shales of the Appalachian Basin is the extent to which a stratified water column persisted leading to anoxic to euxinic bottom waters. The very high organic carbon contents observed in these shales (as high as 15% in some intervals) suggest non-normal marine conditions. The organic matter in these shales is typically Type II, predominated by bituminite (altered algal and bacterial matter)

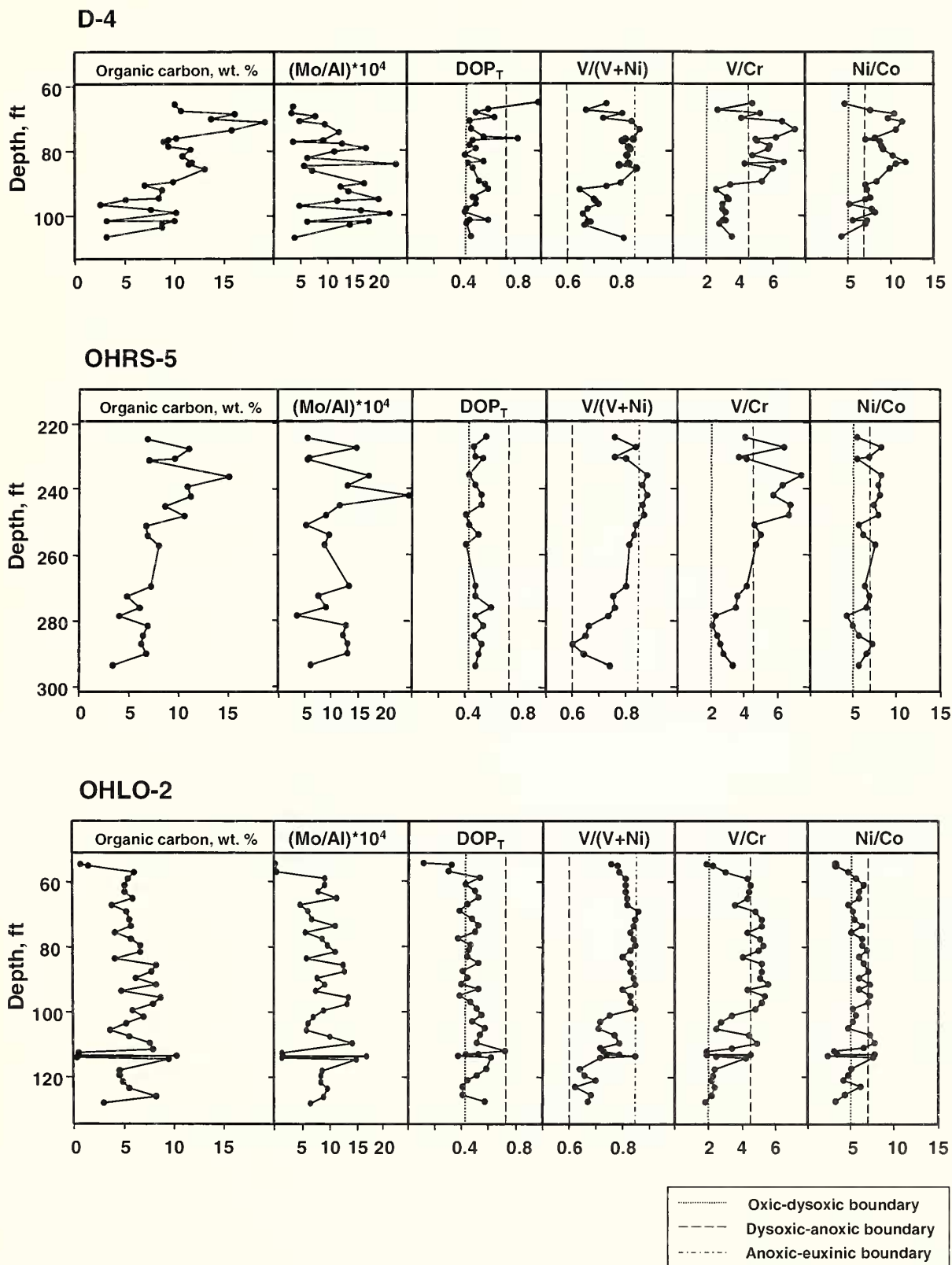


Figure 7. Stratigraphic variations in organic carbon (wt. %) and redox proxies for the three cores in transect B-B' (D-4, OHRS-5, and OHLO-2). Redox thresholds based on values in Figure 4.

**Table 1.** Enrichment factors (EF) for selected trace elements for samples from cores through the Cleveland Shale Member along transects A–A' and B–B'.

Element	Average* Shale	Average** Black Shale	Transect A–A'					Transect B–B'	
			T-16 (n = 12)	D-10 (n = 17)	D-6 (n = 19)	KEP-5 (n = 16)	D-4 (n = 28)	OHRS-5 (n = 21)	OHLO-2 (n = 40)
Co (ppm)	19	10	20	20	19	22	17	18	18
(Co/Al) *10 <sup>4</sup>	2.1	1.4	2.6	2.5	2.4	2.5	2.2	1.8	2.0
EF		0.7	1.2	1.2	1.1	1.2	1.1	0.9	0.9
Cr (ppm)	90	100	164	160	167	198	104	107	97
(Cr/Al) *10 <sup>4</sup>	10.2	14.3	21.6	19.8	20.6	22.5	13.7	11.1	11.0
EF		1.4	2.1	1.9	2.0	2.2	1.0	1.1	1.1
Cu (ppm)	45	70	124	104	103	99	79	60	46
(Cu/Al) *10 <sup>4</sup>	5.1	10.0	16.4	12.9	12.7	11.3	10.4	6.2	5.2
EF		2.0	3.2	2.5	2.5	2.2	2.0	1.2	1.0
Mo (ppm)	2.6	10	101	100	114	125	82	87	71
(Mo/Al) *10 <sup>4</sup>	0.3	1.4	13.3	12.4	14.1	14.2	10.9	9.0	8.0
EF		4.9	44.5	41.3	46.9	47.3	36.2	29.9	26.7
Ni (ppm)	68	50	162	132	138	138	134	116	99
(Ni/Al) *10 <sup>4</sup>	7.7	7.1	21.4	16.3	16.9	15.7	17.7	12.1	11.2
EF		0.9	2.8	2.1	2.2	2.0	2.3	1.6	1.4
V (ppm)	130	150	713	654	740	883	483	506	391
(V/Al) *10 <sup>4</sup>	14.7	21.4	94.2	80.7	91.2	100.5	63.7	52.5	44.2
EF		1.5	6.4	5.5	6.2	6.8	4.3	3.6	3.0
Zn (ppm)	95	300	527	369	478	503	294	278	368
(Zn/Al) *10 <sup>4</sup>	10.7	42.9	69.6	45.5	58.9	57.2	38.7	28.9	41.6
EF		4.0	6.5	4.3	5.5	5.3	3.6	2.7	3.9

\* Average shale data from Wedepohl (1971); \*\* Average black shale data from Vine and Tourtelot (1970).

with lesser amounts of alginite (preserved algal matter), vitrinite (preserved woody tissue from terrestrial sources), and inertinite (oxidized organic matter of both marine and terrestrial origin) (Rimmer et al., 1993; 2004). Within the Devonian shales, the amount and type of organic matter varies stratigraphically and geographically. For example, increased amounts of terrestrial organic matter are observed in the Cleveland Member as compared to the Huron Member which is lower in the section (Rimmer et al., 2004) and there is also thought to be an increase in terrestrial organic matter toward the north (approaching the deltaic source) as suggested by carbon isotopic data (Maynard, 1981).

For such large amounts of organic matter to accumulate, either productivity had to be very high, or preservation had to occur under optimal conditions (i.e., low oxygen conditions), or both. Based on the C-S-Fe relationships observed in these two transects, it is likely that conditions during accumulation of the Cleveland Member of the Ohio Shale were at least dysoxic and probably anoxic to some degree. The lack of a correlation between carbon and sulfur observed for data from all seven cores (Figures 3 and 8) indicates that conditions were not normal marine, and were possibly anoxic; degree-of-pyritization data for these cores plots mostly in the dysoxic range (Figures 5–7). The trace element data also point to at least dysoxic and possibly anoxic conditions. The data also suggest slightly more reducing conditions in the upper part of the unit than in the lower part, and slightly more oxidizing conditions to the north (OHLO-2).

These observations are consistent with those made previously by Rimmer et al. (2004) who suggested that conditions during accumulation of the Cleveland Member were initially dysoxic to anoxic, but became predominantly anoxic during accumulation of the upper part of the unit. Additional data in that study suggested

that productivity was also high, driven by land-derived nutrients and by phosphorous that was regenerated due to a productivity-anoxia feedback mechanism (a decoupling of organic carbon and phosphorus under anoxic conditions).

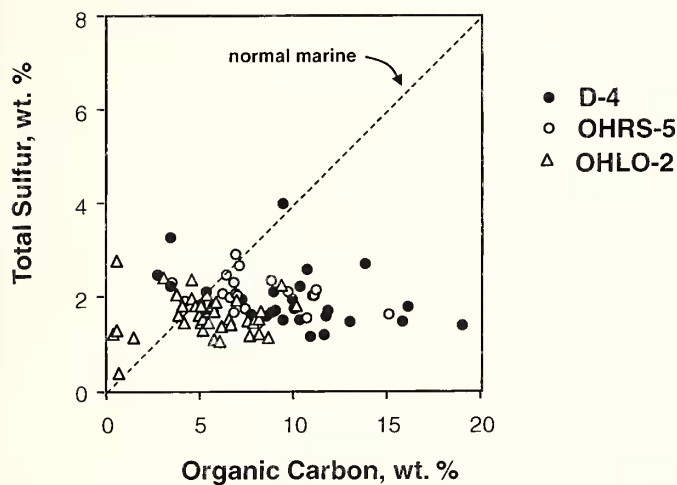
There are indications from this study that conditions were fairly constant (dysoxic for the lower Cleveland, anoxic for the upper Cleveland) in the more distal parts of the basin (i.e., central Kentucky and southern Ohio), but that conditions may have become less extreme towards the north, approaching more proximal facies. In particular, results for core OHLO-2 suggest less reducing conditions, with dysoxic conditions being more prevalent. As these are preliminary data, our future work will focus on additional cores in the northern outcrop belt of Ohio to determine the extent to which trends seen in OHLO-2 are typical.

Another area of interest is the relatively high Mo content of these shales. Recent work by Algeo (2004) using our data for the D-4 core from the UK Devonian Shale Database called upon a drawdown of dissolved Mo in Late Devonian seawater (at the time of accumulation of the upper part of the Cleveland Member) to explain the depletion in Mo at the top of the D-4 core. Further analysis of our core data (for example, KEP-5) and the new data we have collected (for example, OHRS-5) suggest that this trend is not widespread across the entire basin. Thus, whatever the cause of the lower Mo levels seen in the upper Cleveland in some of the cores in the UK Devonian Shale Database, also commented on by Rimmer (2004), it may not be a global or even a basin-wide phenomenon but a situation arising from local conditions.

## Conclusions

Geochemical proxies allow us to infer conditions that existed during accumulation of the Cleveland Member. Based on the data





**Figure 8.** Carbon-sulfur relationships for the Cleveland Member in transect B-B'. The dashed line shows the typical S-C relationship for normal marine sediments (based on Berner and Raiswell, 1983).

from seven cores across the Devonian outcrop belt of the Appalachian Basin, we present the following salient conclusions:

1. Our results indicate stratigraphic and geographic variations in organic carbon content. Within the outcrop belt of Kentucky, the lower Cleveland contains less than 10% organic carbon, with the lower part of the KEP-5 core containing approximately 5%. The upper Cleveland is richer, containing 10 to 15% organic carbon. Moving north into Ohio, organic carbon contents decrease to 10% or less, with no discernable stratigraphic trends in OHLO-2.
2. Conditions during accumulation of the lower part of the Cleveland may have been slightly better oxygenated (dysoxic) compared with the upper parts of the unit (anoxic). This is demonstrated by vertical variations in  $DOP_T$ ,  $V/Cr$ , and  $Ni/Co$ .  $V/(V+Ni)$  ratios indicate more reducing conditions for all cores, but are not necessarily consistent with the other redox indicators.
3. Redox conditions also vary from core to core, suggesting local fluctuations may have been important. Overall, more prevalent anoxic conditions are indicated for the T-16 core than for the KEP-5 core; results for the OHLO-2 core suggest that there were more prevalent periods of dysoxic or, at times, even oxic conditions.
4. Mo contents, while generally high, are not inconsistent with levels previously ascribed to dysoxic conditions. A decrease in Mo content is seen in the upper part of the Cleveland Member in some cores but not others, suggesting local control on Mo content rather than a global or a basin-wide drawdown of seawater Mo levels during accumulation of the upper Cleveland.

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